Energy 74 (2014) 181–189

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Energetic and exergetic evaluation of residual biomass in a torrefaction process

D.A. Granados*, H.I. Velásquez, F. Chejne

Universidad Nacional de Colombia sede Medellín, Facultad de Minas, Colombia

ARTICLE INFO

Article history:
Received 22 September 2013
Received in revised form
12 May 2014
Accepted 13 May 2014
Available online 11 June 2014

Keywords:
Torrefaction
Energy balances
Residual biomass
Exergy balances
Energy yield
HHV (High Heating Value)

ABSTRACT

A torrefaction process in a TGA (Termo-gravimeter analyzer) for six different types of residual biomass (sugarcane bagasse, banana rachis, rice husk, palm oil fiber, sawdust and coffee waste) was developed in this paper. These six materials were evaluated before and after the torrefaction process through HHV (High Heating Value) and energetic and exergetic balances in order to find a promising solid fuel biomass in a torrefaction process. Torrefaction is a thermal process performed in an inert atmosphere at temperatures between 200 and 300 °C, with residence times lower than 60 min and heating rates lower than 20 °C/min. Its aim is to improve biomass as a solid fuel. In this processing, the lignocellulosic components are degraded (hemicellulose and cellulose are more degraded than lignin), having as result a biomass with a predominant amount of lignin. In this work, the torrefaction process was carried out at a temperature of 250 °C in an inert atmosphere with 10 °C/min of heating rate and a residence time of 30 min. As a result, it was found that the biggest and lowest increases in HHV for torrefied biomass were14.5% and 5.2% for sawdust and palm oil fiber, respectively. Sawdust was found to have the best performance in the torrefaction process evaluated from the energy yield parameter but rice husk was the best biomass in the energetic balances of the process. Energy and exergy balances show that palm oil fiber and banana rachis are the least efficient biomass in the torrefaction process.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass is a promising source of solid fuels that compete with fossil fuels like oil and coal because of its low emission of greenhouse gases and its acceptable performance in thermal processes. Despite the benefits of using biomass in thermal processes, its implementation has a major limitation for projects involving high biomass flows. High humidity and low biomass density reduces the feasibility of the projects as the projects' size increases. This is due to the high cost associated with the transport of large amounts of biomass. It is for this reason that only small and medium scale projects may become the only option for obtaining economic benefits from the transformation of thermal biomass.

The torrefaction process is carried out in inert atmospheres or low amounts of oxygen at temperatures in the range of 200–300 °C and low heating rates (<20 °C/min) [1]. During the torrefaction process a mass loss of up to 40% and an energy loss between 5 and 10% are registered for the biomass and a HHV (High Heating Value) is generated [2–4]. Different authors in the literature have experimentally evaluated the performance of biomass when it is subjected to a torrefaction process with variations in operating parameters [5,6], have evaluated the kinetics to suggest reaction mechanisms [7], and have evaluated the torrefied biomass in a combustion process [8–10], gasification [10–12]and crushing [13–15] to improve the process or the performance of the biomass. In addition to the above experimental studies, other approaches such as developing process models [16,17], mass and energy balances that provide information on process feasibility [18–20] and some cost analysis can be found in the literature [21,22].

Bourgois et al. [5] examined the effect of a thermal process at 260 °C in an inert atmosphere on a pine biomass. Residence times were varied between 15 min and 4 h. The gases generated in the process were examined by chromatography, finding the dominant presence of non-condensable components such as CO, CO_2, O_2 and N_2. The authors concluded that CO generation is instantaneous, so that CO_2 generation is not a product of CO combustion. The torrefied solid was analyzed by monitoring its weight during torrefaction and by ultimate and proximate analysis. In these tests it was found that when the residence time varies between 15 min and 4 h, the mass (20–50%), the amount of hydrogen (0.2–19%) and the

---

* Corresponding author.
E-mail addresses: dagranad@unal.edu.co, dagranad@gmail.com (D.A. Granados), fchejne@unal.edu.co (F. Chejne).

http://dx.doi.org/10.1016/j.energy.2014.05.046
0360-5442/© 2014 Elsevier Ltd. All rights reserved.

amount of oxygen of the biomass (5–40%) decrease. In contrast, the amount of carbon in the torrefied material (4–33%) and lignin (30–200%) increase when the residence time increases. In general, the torrefaction process produces an increase in the biomass HHV of up to 44% and improves hydrophobic characteristics that directly impact the lifetime of the material. These tests were performed only at a process temperature, and the heating rate of the biomass or the particle size used is not mentioned in the article, leaving unrevealed much of the behavior of the material when the temperature and other parameters, such as the fraction of oxygen in the process, are modified. These tests were not conducted under experimental design so they only evaluated the impact of a parameter in the process and, therefore, the effect of the other variables in the results cannot be concluded with certainty.

In a later work, Bourgois et al. [6] performed experimental tests similar to those of previous work [5], with the same operating parameters unspecified such as particle size and heating rates and with the difference that the residence time was kept constant and the temperature varied in the range of 240–290 °C. The trends found in the behavior of parameters, such as mass loss, oxygen, hydrogen and lignin, were very similar to those found in previous work. It is noteworthy that the same shortcomings noted in previous work were evidenced again.

Pentananunt et al. [2] evaluated the final characteristics of the torrefied biomass such as proximate and ultimate analysis, and density, but with an additional component corresponding to the performance analysis of the material roasted in a combustion process. In the torrefaction tests, the temperature and residence times were varied from 250 to 270 °C and 2–3 h, respectively. This study found similar results to those found in the works of Bourgois et al. [5,6], in terms of the reduction of hydrogen and oxygen, and increased carbon when the process temperature and the residence time increase. In the combustion tests conducted with torrefied wood and charcoal, the findings were that torrefied biomass shows better performance because it generates less dense smoke, less soot and higher speeds in combustion than virgin biomass. The study does not mention the type of wood used for the torrefaction process.

W-H Chen et al. [23,24] evaluated the torrefaction process in a TGA (Termo-gravimeter analyzer) with four kinds of biomasses with the aim to study the behavior of lignocellulosic structure after thermal process. In this work it was found that hemicellulose is almost completely decomposed, but cellulose and lignin are partially decomposed. They also studied the kinetics of cellulose, hemicelluloses and lignin for different temperatures in an isothermal torrefaction process [23]. They found the kinetic parameter for different ranges of temperature and proposed a reaction order for each reaction in the components. Additionally, they propose a model to predict biomass decomposition from the decomposition of each component. This model has been controverted by different authors because neither synergic effects nor the catalytic effect of ash are considered.

Fisher et al. [10] performed torrefaction tests with willow wood with sizes ranging between 5.6 and 9.5 mm in order to evaluate its performance during the combustion and gasification process. The torrefaction is carried out with heating rates of 5 °C/min from room temperature to 150 °C and maintained there for 45 min. Subsequently, the heating continues with the same heating rate until reaching the process temperature which varies between 270 and 290 °C and it is maintained at this temperature for between 38 and 41 min. Differences in reactivity during the combustion and gasification between torrefied biomass and virgin biomass have been found. The difference in reactivities between these biomasses with longer residence times and higher processing temperatures was evident.

S-W Park et al. [25] evaluated the performance of a torrefied biomass with different operational conditions in a torrefaction process, and in a co-combustion process with coal. In this work low-temperature and several torrefaction processes were developed and blended later with coal for co-combustion tests. The biomass with several torrefaction processes was more reactive than the low-torrefied biomass. This behavior is due to the complete decomposition of some components like hemicelluloses and cellulose in the pre-treatment process because, during combustion process, some shoulders are seen for low-temperature torrefied biomass due to the components that were not decomposed in the torrefaction process.

Repellin et al. [14] evaluated the performance of torrefied biomass in terms of energy consumption in a shredding process. The torrefaction process was carried out with biomass pellets, varying residence time (5–60 min) and process temperatures (180–260 °C), and subsequently crushing the pellets in a ball mill to a particle size of less than 200 μm. Once this particle size was reached, the energy consumed in the grinding process was measured and compared with other virgin and torrefied biomasses with different operating conditions. It was found that with biomass torrefied at higher temperatures significant reductions (93%) in energy consumption can be obtained.

Some authors have addressed the issue of biomass torrefaction by performing mass, energy and exergy balances, trying to add its energy and exergy viability to the obvious benefits of the process.

Prins et al. [18] evaluated the torrefaction process bound to a gasification process. To carry out the analysis of torrefied biomass performance under different operating conditions, different configurations were evaluated combining the torrefaction processes and gasification. One of the tested combinations considers the use of volatiles produced in the torrefaction as an energy part of the gasification. After an exergetic analysis of the different configurations, the authors concluded that when a torrefaction pretreatment is linked to the gasification process, where part of the energy of the process is provided by the exhaust gases and volatiles from the gasification process and torrefaction, respectively, it is possible to improve the performance of the biomass in the gasification process as well as the overall efficiency of the process. These analyses were conducted theoretically and, therefore, the authors suggest experimental verification.

Yan et al. [20] performed mass and energy balances for biomass torrefaction process under two different operating conditions and the same residence time. The torrefied biomass (pine) showed the trends highlighted by different authors in their experimental work when the temperatures increase. In these balances, the heats of reaction in each solid biomass were calculated and the authors concluded that these were totally independent from process temperatures.

Models have been developed trying to describe the torrefaction process. Ratte et al. [17] developed one of the most complete models found so far in the literature for biomass torrefaction process. This model considered two phases inside the reactor: a phase composed by biomass particles and a continuous phase composed of 11 species for the gas entering the reactor and generated in the process. The modeling process is for a continuous process and eight reactions were considered during the torrefaction process. Although the validations performed with experimental data have acceptable agreement with the results of the model, some simplifications in the simulations limited the accuracy of the results and forced the authors to improve them to increase the model's performance. One of the phenomena that occurs during the torrefaction process and which is not considered in the model is the condensation of condensable volatiles or tar generated in the process.

This work was focused on finding a potentially promising solid fuel from residual biomasses when they are treated thermally in a torrefaction process in TGA. For this purpose, the residual biomasses were torrefied at 250 °C and 30 min of residence time and evaluated with energy and exergy analysis and energy experimental parameters.

2. Experimental setup

Six biomasses were torrefied in APT STA 1600 LINSEIS-type TGA located in the Energy Laboratory of the National University of Colombia of Medellín. All the biomasses were dried at ambient temperature with a temperature average of 23 °C and 400 W/m^2 of solar average radiation for 12 h and crushed to obtain a particle size of 150 μm (mesh 100). Two experimental runs were done for each biomass with an approximate amount of 10 mg. The torrefaction process was developed in an inert atmosphere of nitrogen with an initial dry heating of up to 110 °C during 10 min, followed by a last heating until the process temperature reached 250 °C, and this operational condition was kept for 30 min (Fig. 1). These operational conditions were selected with the aim of work with middle process temperature, found as optimal for biomass by Prins et al. [26,27]. Both heatings were done with a slow heating rate of 10 °C/min. A natural cooling was achieved until reaching ambient temperature for each biomass. Nitrogen was supplied at a rate of 50 ml/min in order to ensure an inert atmosphere.

Two runs for each biomass were done and during the experimental runs the mass was monitored. An initial run without material was done with the aim to correct and eliminate errors by external effects in the thermo-gravimetric analysis. The experimental setup used for the thermal process is shown in Fig. 2.

All biomasses were characterized before the thermal process by ultimate and proximate analysis (Tables 1 and 2). In the proximate analysis, the biomass HHV was obtained experimentally by calorimeter pump. After the thermal process, all biomasses were characterized only by ultimate analysis (Table 4) because with the reduced amount of material the proximate analysis could not be done. All the information shown in the analysis is the average of three analyses done for each biomass. From ultimate information, HHV was obtained through the empirical correlations for biomass suggested by Friedl et al. [28] and compared to experimental HHV. This correlation is shown in equation (1) in which elemental amounts from ultimate analysis are used.

$$\mathrm{HHV(kJ/kg)} = 3.55\mathrm{C}^2 - 232\mathrm{C} - 2230\mathrm{H} + 51.2\mathrm{C}^*\mathrm{H} + 131\mathrm{N} + 20600 \quad (1)$$

As shown in Tables 1 and 2, the differences between HHV calculated by correlation and experimental HHV are in a range of 420–1600 kJ/kg (2.8–9.7%). These differences will be taken into account in order to analyze the results after the thermal process.

3. Results

As mentioned in the previous chapter, the biomasses were heated at 10 °C/min until reaching a temperature of 110 °C during 10 min and then heated again at 10 °C/min until reaching the torrefaction process temperature of 250 °C and maintained at this temperature for 30 min. The kiln was turned off and natural cooling until reaching room temperature was done for the biomass and, after this, the biomass was extracted. Ultimate analysis was done for the torrefied biomasses and the HHV was calculated according to the correlation mentioned above [28].

The mass loss in all runs was monitored and recorded with maximum errors of 5% between runs of the same materials. The representative results of each run in the process are shown in Fig. 3. In this figure it can be observed that the dry process with 10 min is enough to remove the water in the biomass. An interesting behavior in the second heating process was that all biomass starts decomposition around 180–190 °C. This is in accordance with literature information about decomposition temperatures of biomass components [29]. In this temperature range (180–190 °C) the hemicelluloses start their decomposition producing volatiles like CO_2, CO and low fractions of liquids like acetic acid [27]. In these hemicelluloses' decomposition, banana rachis, coffee waste and palm oil fiber present a fast mass loss probably due to a high amount of hemicellulose.

The banana rachis was dried at ambient temperature too, but its moisture was very high (12% approximately) resulting in a larger fictitious mass loss in this material. As results of these experimental runs, sugarcane bagasse was the material that exhibited the least mass loss with around 13.5%, followed by rice husk and sawdust with 17% and 20%, respectively, neglecting the initial moisture. Coffee, palm oil fiber and banana rachis were the materials with a high mass loss of 27, 34 and 35%, respectively, neglecting the initial moisture. In the torrefaction process, those materials that have a great mass loss during the thermal process are not a good option to produce solid fuels. Fig. 3 shows some slope changes during the process as a result of decomposition of cellulose and lignin, which are decomposed into smaller quantities than hemicelluloses. This

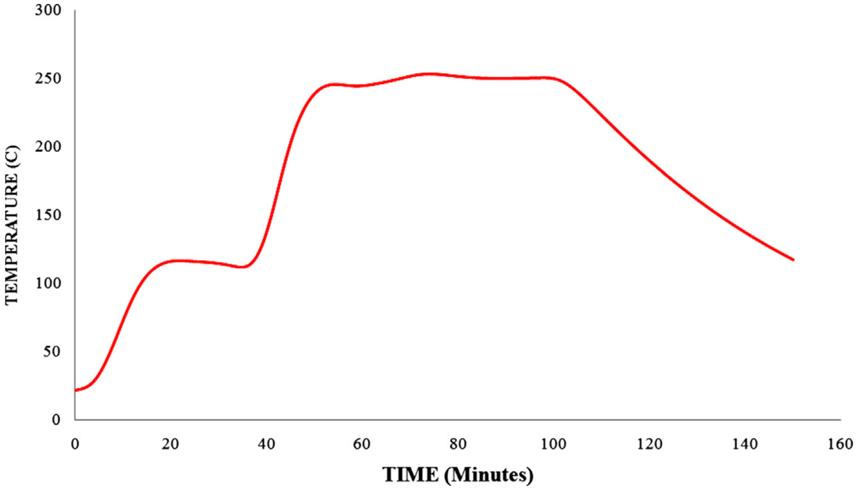

Fig. 1. Temperature ramp utilized for the torrefaction process for all biomasses.

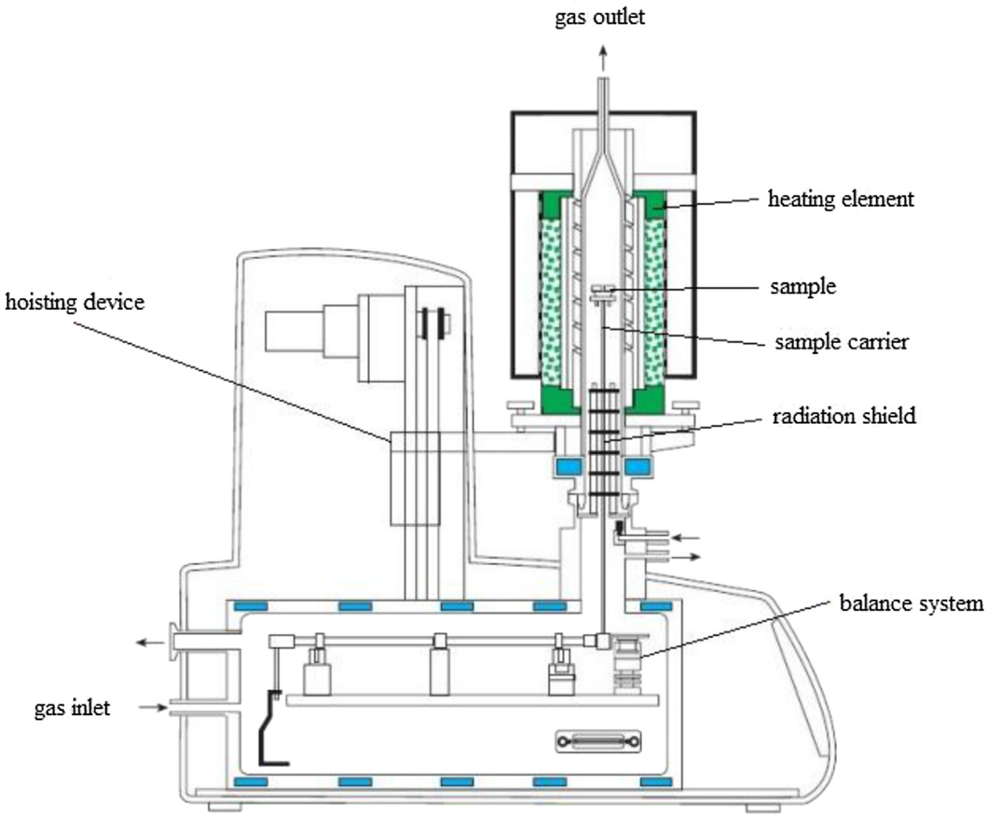

Fig. 2. TGA scheme used in the experimental torrefaction process of biomass (250 °C, 30 min).

fact is observed in the different slopes that are present in all the thermal process.

One of the main features in the torrefaction process is that mass loss is higher than energy loss, leading to a densification of biomass and increasing the HHV. Results of ultimate analyses for all torrefied biomasses (Table 3) are shown and their new HHVs were obtained using the above correlation [28]. The values shown in Table 3 are the average of three analyses.

A comparison between mass before and after the torrefaction process was developed in order to clarify the effect that the thermal process produces over lingo-cellulosic materials (Table 4). The HHV comparison was done with the theoretical ones in order to reduce the margin of error.

Table 1
Ultimate analysis and theoretical HHV of raw biomass (%w/w).

Biomass	C	H	N	O	Theoretical HHV (kJ/kg)
Palm oil fiber	42.5 ± 0.4	6.4 ± 0.3	1 ± 0.1	42.6 ± 0.7	16,953 ± 899
Banana rachis	32.5 ± 0.3	4.6 ± 0.3	1.6 ± 0.5	36.4 ± 1.1	14,388 ± 969
Sugarcane bagasse	42.5 ± 1.1	5.4 ± 0.4	0.4 ± 0.1	47.6 ± 1.7	16,267 ± 1616
Rice husk	33.6 ± 1.0	4.0 ± 0.9	2.2 ± 0.4	38.5 ± 2.3	15,047 ± 2471
Sawdust	45.2 ± 0.1	5.7 ± 0.2	0.4 ± 0.2	45.7 ± 0.5	17,936 ± 590
Coffee waste	44.6 ± 0.6	6.3 ± 0.5	2.7 ± 0.4	41.8 ± 1.6	18,012 ± 1577

Table 2
Proximate analysis and experimental HHV of raw biomass (% w/w).

Biomass	Moisture	Ash	Fixed carbon	Volatiles	Experimental HHV (kJ/kg)
Palm oil fiber	4.2 ± 0.2	7.3 ± 0.1	9.9 ± 0.6	78.3 ± 0.6	18,448 ± 172
Banana rachis	5.1 ± 0.1	24.7 ± 0.4	11.6 ± 0.5	58.4 ± 0.8	13,479 ± 92
Sugarcane bagasse	5.2 ± 0.2	3.9 ± 0.6	8.3 ± 0.3	82.5 ± 0.5	16,920 ± 340
Rice husk	5.1 ± 0.1	21.5 ± 0.2	17.1 ± 0.4	56.5 ± 0.4	14,627 ± 408
Sawdust	6.5 ± 0.2	2.8 ± 0.3	2.2 ± 0.2	88.3 ± 0.3	18,503 ± 660
Coffee waste	4.4 ± 0.2	5.3 ± 0.2	11.6 ± 0.5	78.6 ± 0.2	16,412 ± 537

To clarify the effect generated by the torrefaction process, a bargraph illustrates the change in the HHV of the biomass before and after the process (Fig. 4). It is clear that the thermal process generates better solids with higher HHV.

The biggest increase in the HHV of the biomasses evaluated was shown by sawdust with 14.5%, followed by coffee waste with 14.1%. The lowest increase in HHV was presented by the palm oil fiber with only 5.2%. Besides observing HHV increases, the loss of mass must be related to the analysis, to generate a parameter that relates HHV with mass and to obtain the energy available in the torrefied solid. This parameter is known as "*energy yield*" and is shown in equation (2). A graphical result is shown in Fig. 5.

$$\text{Energy Yield} = \frac{\text{Total Energy of torrefied biomass}}{\text{Total Energy of raw biomass}} = \frac{\text{HHV}_{\text{torrefied biomass}}\text{*Weight of torrefied biomass}}{\text{HHV}_{\text{raw biomass}}\text{*Weight of raw biomass}} \tag{2}$$

Table 3
Ultimate analysis for torrefied biomass (250 °C, 30 min).

Biomass	%C	%H	%N	%O	Theoretical HHV (kJ/kg)
Palm oil fiber	44.3 ± 3.7	4.1 ± 0.3	2.9 ± 0.3	41.1 ± 1.5	17,843 ± 1216
Banana rachis	36.2 ± 1.5	3.3 ± 0.8	3.0 ± 0.3	32.6 ± 1.9	15,970 ± 2160
Sugarcane bagasse	44.0 ± 2.4	4.1 ± 0.5	1.1 ± 0.2	46.7 ± 1.7	17,519 ± 1735
Rice husk	40.0 ± 0.9	4.3 ± 0.1	1.3 ± 0.1	32.7 ± 1.1	16,422 ± 853
Sawdust	47.8 ± 0.9	4.6 ± 0.1	1.1 ± 0.1	39.3 ± 1.1	20,534 ± 706
Coffee waste	51.7 ± 0.6	4.8 ± 0.3	3.2 ± 0.4	35.6 ± 1.3	20,560 ± 1138

Table 4
Mass and HHV of biomass before and after the torrefaction process.

Biomass	Solid HHV (kJ/kg)			Solid mass (mg)		
	Inlet	Outlet	Increase (%)	Inlet	Outlet	Mass loss (%)
Palm oil fiber	16,953 ± 899	17,843 ± 1216	5.2%	10.83 ± 0.01	6.6 ± 0.01	38%
Banana rachis	14,388 ± 969	15,970 ± 2160	11.0%	10.58 ± 0.01	6.0 ± 0.01	42%
Sugarcane bagasse	16,267 ± 1616	17,519 ± 1735	7.7%	11.07 ± 0.01	9.0 ± 0.01	18%
Rice husk	15,047 ± 2471	16,422 ± 853	9.1%	10.63 ± 0.01	8.2 ± 0.01	22%
Sawdust	17,936 ± 590	20,534 ± 706	14.5%	10.43 ± 0.01	7.7 ± 0.01	25%
Coffee waste	18,012 ± 1577	20,560 ± 1138	14.1%	10.60 ± 0.01	7.3 ± 0.01	30%

The energy yield represents the available energy ratio between raw and torrefied biomass, and indicates a promissory biomass to be transformed in a torrefaction process. In this case, sugarcane bagasse and sawdust are the promising biomasses to be transformed by a torrefaction process and obtain a solid fuel with better characteristics. Banana rachis had the lowest performance in the torrefaction process, showing only 0.63 in the energy yield parameter.

4. Mass and energy balances

In a torrefaction process of biomass, gases, liquids and solids are obtained as main products. The main species in these products are CO_2 and CO, acid acetic and a torrefied solid, respectively [30]. To develop the mass and energy balances, the initial moisture in the biomass was separated, taken in separately as liquid water, and expelled of the process as steam water. The inert gas necessary for the process was considered in the process as additional specie in the balances. In order to simplify the mass and energy balances, the condensable and non-condensable gases were grouped into global specie called volatiles (Fig. 6).

With these products and flows known, the mass and energy balances can be performed. The HHV [28] and heat capacities [31]of raw and torrefied biomass were obtained from empirical correlations. The heat capacity of each biomass was found from the heat capacities of the elemental species in the solid state according to equation (3). It was necessary to express the biomass with a chemical expression of the elemental species ($C_xH_yO_z$).

$$c_p(\mathrm{J/mol^*K}) = (7.524^*x) + (9.614^*y) + (16.720^*z) \tag{3}$$

The enthalpy of formation of raw and torrefied biomass for energy balances are calculated through the Hess law, having the calculated HHV (enthalpy of reaction) in a fictitious combustion reaction and the enthalpy of formation of products in this reaction according to equation (4). These enthalpies of formation, heats capacities and chemical formulas for all biomasses are shown in Tables 5 and 6. This methodology has also been used in some published works such as Wei Yan [20].

$$\mathrm{C}_x\mathrm{H}_y\mathrm{O}_z(\mathrm{s}) + \left(1 + \frac{y}{4} - \frac{z}{2}\right)\mathrm{O}_2(\mathrm{g}) \xrightarrow{\Delta H_\mathrm{R}} \mathrm{CO}_2(\mathrm{g}) + \left(\frac{y}{2}\right)\mathrm{H}_2\mathrm{O}(\mathrm{L}) \tag{4}$$

From the above information, energy balances were performed and the enthalpy of reaction for each torrefaction reaction of each biomass was found as is shown in equation (5), and the heat request for the torrefaction process was also found, as shown in equation (6). For energy balance calculations, it was assumed that input streams consist of raw biomass, nitrogen and liquid moisture, and outlet streams consist of volatiles, nitrogen, steam and a torrefied biomass. It was assumed that volatiles are composed of CO_2 and acetic acid according with previous experimental works [20,32]. The CO_2 and acetic acid are presented in proportions of 74% and 26%, respectively, in the volatiles [20,32]. This has been verified experimentally by Yan et al. [20] for temperatures of 260 °C.

$$\mathrm{C}_x\mathrm{H}_y\mathrm{O}_z(\mathrm{s}_1) \xrightarrow{\Delta H_\mathrm{R}} \mathrm{C}_x\mathrm{H}_y\mathrm{O}_z(\mathrm{s}_2) + \mathrm{CO}_2 + \text{Acetic Acid} + \mathrm{H}_2\mathrm{O} \tag{5}$$

$$\left(m_{\mathrm{s}_2}\Delta H^{\circ}_{f_{s_2}}\right)_{\mathrm{out}} + \sum_{i=1}^{n} m_i\left(\Delta H^{\circ}_{f_i} + c_\mathrm{p}\Delta T\right) - \left(m_{\mathrm{s}_1}\Delta H^{\circ}_{f_{s_1}}\right)_{\mathrm{in}} = Q \tag{6}$$

The results of the energy balances are presented in Table 7. A summary of the mass and energy balances for the wood torrefaction process is presented in Fig. 7. This graph shows that the volatile gases contain 8% of the initial energy of the biomass. This energy could be used later in a biomass pre-heater or in the gas recirculation to the reactor and provide a portion of the energy required in the system.

Future assessments quantifying the species in the gas outlet and involving the amounts of hemicellulose, cellulose and lignin are under development.

5. Exergy balances

Exergy is defined as the maximum potential work that can be obtained from a material flow, heat transfer or work to bring this stream or system to environmental conditions; conditions that are associated with the dead state where the currents are in chemical, thermal and mechanical equilibrium with the atmosphere. Among the different forms of exergy, for this process, only those relevant, such as thermal, work and material exergies, are quantified, and smaller amounts, such as the kinetic and potential exergy, are neglected. According to the above, the specific exergy (J/mol) was calculated from equation (7) for each stream [33]:

$$b^{\mathrm{t}} = b^{\mathrm{ch}} + b^{\mathrm{ph}} \tag{7}$$

where b^{ch} and b^{ph} are the chemical and physical exergy, respectively. The chemical exergy for a gas mixture or non-combustible solids is obtained from equation (8) and for a fuel ($b^{\mathrm{ch}}_{\mathrm{F}}$) is calculated by equation (9) [33]:

$$b^{\mathrm{ch}} = \sum x_i b^{\mathrm{ch}}_i + \sum x_i \ln(x_i) \tag{8}$$

$$\begin{aligned} b^{\mathrm{ch}}_{\mathrm{F}} = {} & \overline{\mathrm{HHV}}(T_0, P_0) - T_0\left[s_{\mathrm{DAF}} + \nu_{\mathrm{O}_2}s_{\mathrm{O}_2} - \nu_{\mathrm{CO}_2}s_{\mathrm{CO}_2} - \nu_{\mathrm{H}_2\mathrm{O}}s_{\mathrm{H}_2\mathrm{O}} - \nu_{\mathrm{SO}_2}S_{\mathrm{SO}_2} - \nu_{\mathrm{N}_2}s_{\mathrm{N}_2}\right] \\ & + \left[\nu_{\mathrm{O}_2}b^{\mathrm{ch}}_{\mathrm{O}_2} + \nu_{\mathrm{CO}_2}b^{\mathrm{ch}}_{\mathrm{CO}_2} + \nu_{\mathrm{H}_2\mathrm{O}}b^{\mathrm{ch}}_{\mathrm{H}_2\mathrm{O}} + \nu_{\mathrm{SO}_2}b^{\mathrm{ch}}_{\mathrm{SO}_2} + \nu_{\mathrm{N}_2}b^{\mathrm{ch}}_{\mathrm{N}_2}\right] \end{aligned} \tag{9}$$

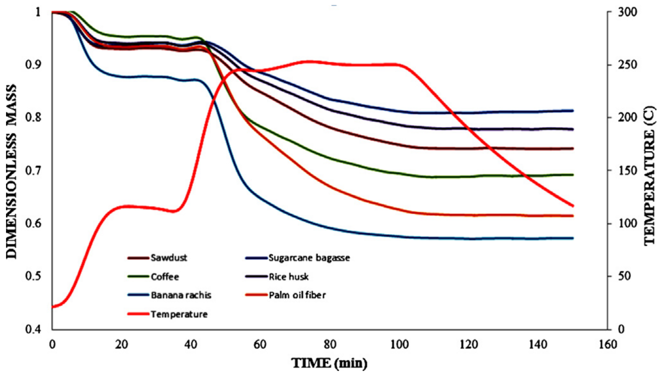

Fig. 3. Mass loss during torrefaction process of biomass (250 °C, 30 min).

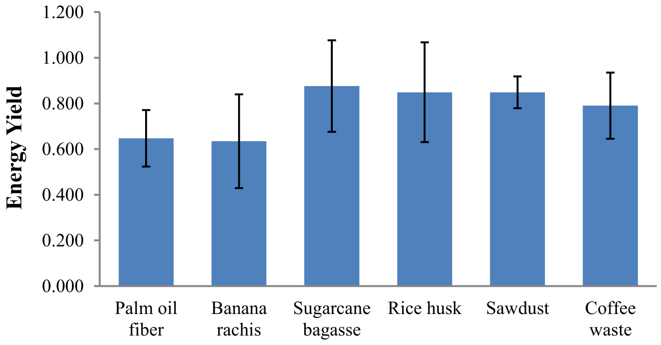

Fig. 5. Energy yield for torrefaction process at temperature of 250 °C for 30 min.

where x_i and b_i^{ch} in equation (8) are the molar fraction of the i specie in the gas stream and the chemical exergy of the i specie in the stream. In equation (9), the chemical exergy of a solid fuel is obtained considering the products of a combustion reaction of this fuel. In this equation,ν_i is the molar fraction of the i specie, s_i is the entropy of the i specie,T_0 and P_0 are the temperature and pressure of the reference state, $\overline{HHV}$ is the highest heating value of the biomass, and b_i^{ch} is the chemical exergy of the i specie. The term s_{DAF} is defined as follows:

$$s_{DAF} = c\left[37.1653 - 31.4767\exp\left(-0.564682\frac{h}{c+n}\right) + 20.1145\frac{o}{c+n} + 54.3111\frac{n}{c+n} + 44.6712\frac{s}{c+n}\right] \tag{10}$$

where h, n, c and o are the amounts of hydrogen, nitrogen, carbon and oxygen in the elemental analysis. Physical exergy of a gas stream or solid was calculated with equation (11):

$$b_{ph} = (h_i - h_{0_i}) - T_0(s_i - s_{0_i}) \tag{11}$$

where h_i and s_i are the enthalpy and entropy of the specie i in the stream andh_{0_i} ands_{0_i} are the enthalpy and entropy of the specie i in the stream in the reference state.

With these expressions, the total exergy for each process can be obtained considering the inlet and outlet streams shown in Fig. 6. The chemical exergy of the biomass and biochar were calculated in agreement with equation (9). The irreversibilities and efficiency in all processes were found in accordance with equations (12) and (13):

$$I = b_{in} - b_{out} \tag{12}$$

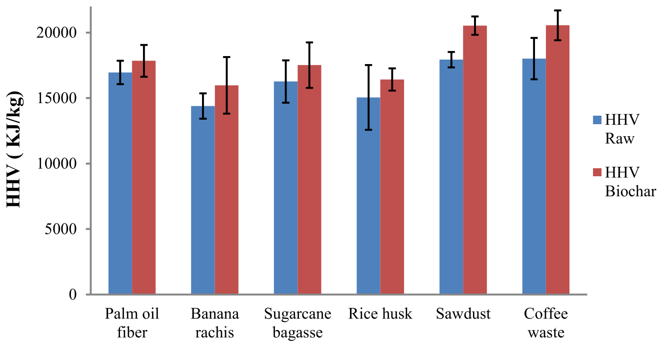

Fig. 4. HHV of biomass before and after the torrefaction process.

$$\Psi = \frac{b_{out}}{b_{in}} \tag{13}$$

where b_{in} is represented by the exergy of the biomass, moisture and inert gas, and b_{out} is represented by the exergy of the biochar, volatiles (condensable and non-condensable) and the inert gas. The exergy related with heat input to realize the torrefaction process is expressed by equation (14):

$$b_Q = \left(1 - \frac{T_0}{T_p}\right)Q_r \tag{14}$$

where T_p is the process temperature and Q_r is the heat of reaction shown in Table 7. The exergy balances were done from mass and energy balances, and the exergies of all streams can be seen in Table 8. The values shown in Table 8 are obtained in relation to the amount of raw biomass and the units shown are kJ/kg raw biomass.

In this table, it is clear that the contribution of H_2O in the inlet stream is negligible, and the greatest contribution is given by the chemical exergy of the raw biomass. In the outlet stream, something similar happens with H_2O, acetic acid and CO_2, which have low contribution to the total exergy in the stream. The exergy input and output of the biomass are shown in Fig. 8 for the purpose of

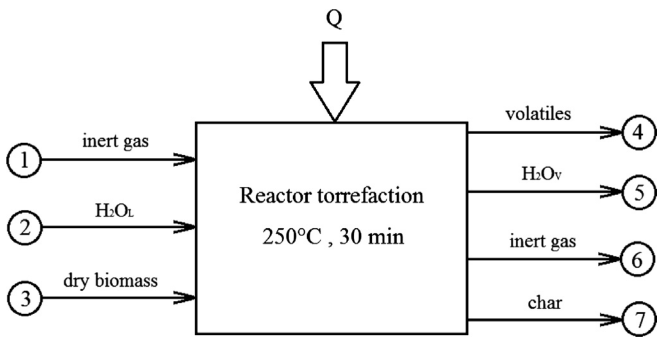

Fig. 6. Mass and energy balance for torrefaction process at a temperature of 250 °C for 30 min.

Table 5
Chemical formula, enthalpy capacity and enthalpy of formation for raw biomasses.

Biomass	Raw biomass				
	$C_xH_yO_z$			Heat capacity	Enthalpy of formation
	x	*y*	*z*	kJ/kg K	kJ/kg
Palm oil fiber	1.00 ± 0.02	1.80 ± 0.01	0.90 ± 0.01	1.45 ± 0.11	−8257 ± 899
Banana rachis	1.00 ± 0.02	1.70 ± 0.01	1.40 ± 0.01	1.41 ± 0.12	−9189 ± 969
Sugarcane bagasse	1.00 ± 0.06	1.50 ± 0.01	0.90 ± 0.01	1.41 ± 0.29	−6786 ± 1617
Rice husk	1.00 ± 0.05	2.50 ± 0.02	4.40 ± 0.01	1.32 ± 0.27	−7030 ± 2471
Sawdust	1.00 ± 0.01	1.50 ± 0.01	0.80 ± 0.01	1.36 ± 0.04	−5868 ± 589
Coffee waste	1.00 ± 0.03	1.71 ± 0.01	0.70 ± 0.01	1.43 ± 0.18	−7544 ± 1576

Table 6
Chemical formula, enthalpy capacity and enthalpy of formation for torrefied biomasses.

Biomass	Torrefied Biomass				
	$C_xH_yO_z$			Heat capacity	Enthalpy of formation
	x	*y*	*z*	kJ/kg K	kJ/kg
Palm oil fiber	1.00 ± 0.17	1.10 ± 0.01	0.80 ± 0.01	1.24 ± 0.23	−5004 ± 1216
Banana rachis	1.00 ± 0.08	1.10 ± 0.03	1.20 ± 0.01	1.24 ± 0.28	−7165 ± 2161
Sugarcane bagasse	1.00 ± 0.13	1.10 ± 0.02	0.90 ± 0.01	1.22 ± 0.32	−3890 ± 1735
Rice husk	1.00 ± 0.03	1.30 ± 0.01	1.00 ± 0.01	1.31 ± 0.20	−8592 ± 852
Sawdust	1.00 ± 0.04	1.20 ± 0.01	0.70 ± 0.01	1.31 ± 0.27	−5229 ± 706
Coffee waste	1.00 ± 0.02	1.12 ± 0.01	0.52 ± 0.01	1.26 ± 0.16	−5304 ± 1137

Table 7
Mass and energy balance for torrefaction process.

Biomass	Mass in (kg)	Energy (kJ)	Solid mass out (kg)	Energy (kJ)	Heat (Q) (kJ/kg)
Palm oil fiber	1.00 ± 0.01	16,953 ± 930	0.61 ± 0.01	10,884 ± 1752	2320 ± 2091
Banana rachis	1.00 ± 0.01	14,388 ± 996	0.57 ± 0.01	9102 ± 1482	1944 ± 3111
Sugarcane bagasse	1.00 ± 0.01	15,471 ± 1646	0.81 ± 0.01	14,190 ± 2029	2525 ± 3321
Rice husk	1.00 ± 0.01	15,047 ± 2500	0.77 ± 0.01	12,644 ± 703	−2043 ± 3321
Sawdust	1.00 ± 0.01	17,935 ± 624	0.74 ± 0.01	15,195 ± 577	392 ± 1260
Coffee waste	1.00 ± 0.01	18,012 ± 1611	0.69 ± 0.01	14,186 ± 844	1680 ± 2600

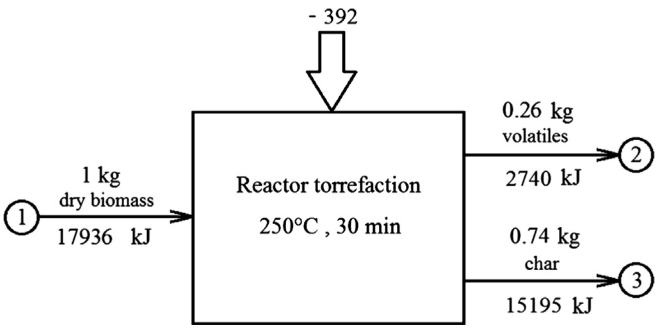

Fig. 7. Mass and energy balance for the torrefaction process of sawdust at a temperature of 250 °C for 30 min.

observing the loss availability in the biochar obtained in the torrefaction process.

The total inlet and outlet exergies in all the process are shown in Fig. 9. In this picture, it can be seen that the irreversibility for the torrefaction of palm oil fiber, banana rachis and coffee waste are bigger than in the other processes. The big amounts of volatiles yielded in these processes cause the irreversibility to increase and a great amount of exergy to be lost in these streams. The energy loss in the exhaust gases can be used either in preheating the inlet biomass or by recirculation directly to the kiln in order to reduce the irreversibilities in the process.

The exergetic efficiency for biomass torrefaction is shown in Fig. 10. This figure shows that torrefaction of sugarcane bagasse, rice husk and sawdust are the most efficient processes. It was expected that when the irreversibility increased, the process efficiency decreased, according to the definition of exergetic efficiency

Table 8
Total exergy of inlet and outlet streams in the process.

	IN (kJ/kg)			OUT (kJ/kg)			
	Biomass	H_2O_L	Q	Biochar	H_2O_V	Acetic acid	CO_2
Palm oil fiber	17,696 ± 959	23 ± 0.1	1906 ± 1725	12,806 ± 880	27 ± 0.2	1043 ± 4	110 ± 1
Banana rachis	14,326 ± 1106	27 ± 0.1	1281 ± 2054	8829 ± 1392	33 ± 0.1	1320 ± 4	139 ± 1
Sugarcane bagasse	16,913 ± 1676	94 ± 0.3	1697 ± 2238	15,069 ± 1664	100 ± 0.3	621 ± 2	133 ± 1
Rice husk	13,454 ± 2528	92 ± 0.3	−1387 ± 2250	12,066 ± 751	98 ± 0.4	768 ± 3	164 ± 1
Sawdust	18,620 ± 652	116 ± 0.4	−165 ± 531	16,381 ± 607	123 ± 0.3	634 ± 2	135 ± 1
Coffee waste	18,528 ± 1641	80 ± 0.3	742 ± 1188	11,993 ± 893	85 ± 0.3	1488 ± 5	318 ± 1

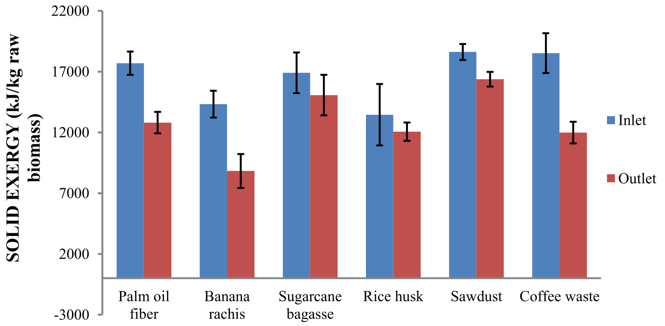

Fig. 8. Solid exergy for biomass torrefaction at a temperature of 250 °C for 30 min.

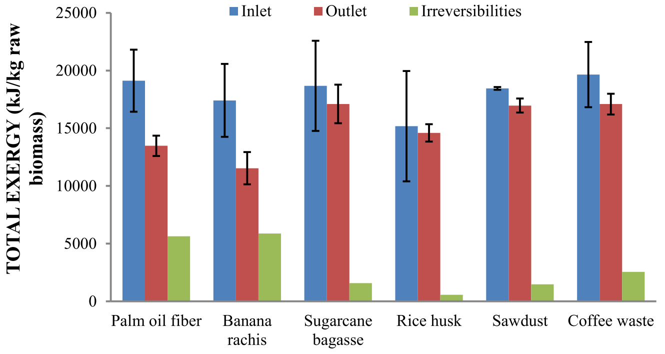

Fig. 9. Total exergy of input and output streams in biomass torrefaction at 250 °C for 30 min.

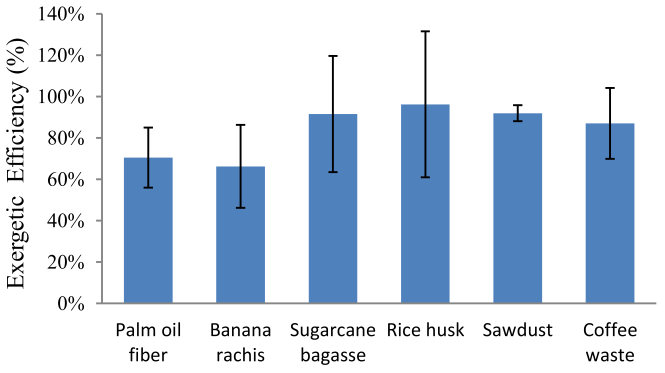

Fig. 10. Exergetic efficiency for biomass torrefaction at 250 °C for 30 min.

in equation (13). This is the reason why the highest efficiencies are found for sugarcane bagasse, rice husk and sawdust, due to their lower irreversibility present in the process.

A dynamic analysis with respect to the input and output exergy depending on a cost ratio R, defined by equation (15), was performed in order to find an optimum operating condition regarding the mass lost in the torrefaction process. This dynamic analysis was done in agreement with equations (16) and (17) and suggests an optimum value for a mass loss in a torrefaction process to obtain a profitable solid fuel from the standpoint of costs of biomass before and after the process.

$$R = \frac{\text{Cost of biochar (\$/kg biochar)}}{\text{Cost of raw biomass (\$/kg raw biomass)}} \tag{15}$$

$$E_1 = R^*(M_{\text{tb}}{}^*\text{HHV}_{\text{rb}}) \tag{16}$$

$$E_2 = R^*(M_{\text{tb}}{}^*\text{HHV}_{\text{tb}}) \tag{17}$$

M_{tb} represents the mass of the biomass at any time, HHV_{rb} and HHV_{tb} represent the HHV of raw biomass and torrefied biomass obtained for any M_{tb}. This latter value was obtained by interpolation between the HHV of raw biomass and the final torrefied biomass. In Fig. 11, E_1 parameter is shown in blue (in web version) lines and E_2 parameter is shown in the green (in web version) line. The intercept point of each blue (in web version) line with the green (in web version) line represents the mass loss optimum for a profitable process. R was set to 1.02, 1.05 and 1.08%, which means an increase in the torrefied biomass cost of 2, 5 and 8% in relation with raw biomass.

The graph was analyzed for the case of sugarcane bagasse, in which it was found that for a ratio of 2, it should have a mass loss of about 5% for a profitable process; for a 1.08 ratio, the mass loss should be approximately 22%. The latter means that the optimum operational conditions depend on the torrefied biomass cost with respect to the biomass cost.

6. Conclusions

In this work, mass and energy balances were performed in order to find a residual agricultural biomass promising for use as a solid fuel in thermal processes. The most promising biomass was sawdust, which had an increase of 14.5%in HHV, from 17.9 MJ/kg in its raw state to 20.5 MJ/kg after processing. In addition to this

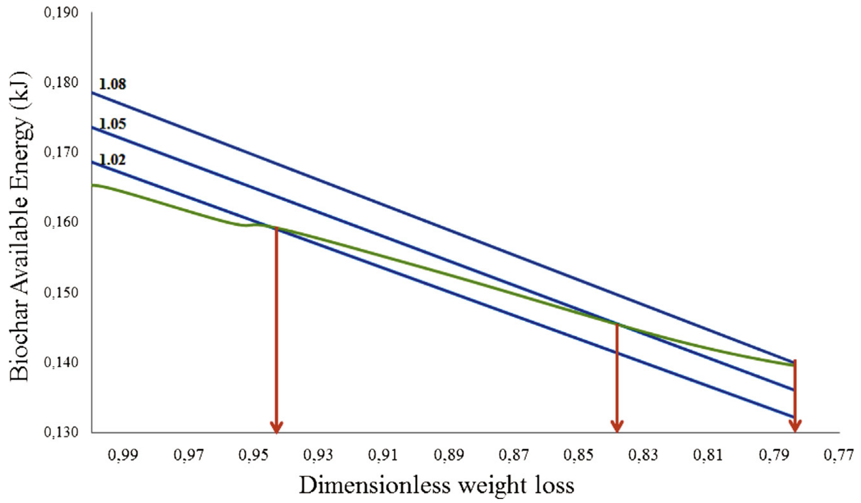

Fig. 11. Optimal operational condition for a cost ratio of 1.02, 1.05 and 1.08 for bagasse torrefaction at 250 °C for 30 min.

increase in energy, less energy intake was required for the thermal decomposition of its structure due to exothermic reactions that took place during the torrefaction process. Rice husk presented an exothermic heat of reaction of 1541 kJ during the torrefaction process, but performing the analysis by means of the "energy yield" indicator does not have as good results compared with sawdust.

Exergy balances for the torrefaction process of all the biomass evaluated were performed. As was expected, energy availability of the biochar obtained is less than that of raw biomass, leading to losses during the process. In addition, the irreversibility present in the torrefaction of sugarcane bagasse, rice husk and sawdust is lower than for the other processes, the irreversibility of torrefaction of rice husk being the lowest and the most efficient.

Analyses of optimal operating conditions were performed using cost ratio between the biochar obtained and the untreated biomass in order to find the optimal biomass mass loss for a viable torrefaction process. We found that for a cost ratio of 1.08, the biomass mass loss can be of up to 22%. It was found experimentally that the torrefaction process is a way to transform the residual biomass and improve moisture content, biomass density and other properties in order to use it in thermal processes.

Acknowledgments

The authors wish to thank the Departamento Administrativo de Ciencia, Tecnología e Innovación (COLCIENCIAS) (Colombian Administrative Department of Science, Technology and Innovation) for financial support.

References

[1] Basu P. Biomass gasification and pyrolysis: practical design and theory; 2010. pp. 64–96.

[2] Pentananunt R, Rahman ANMM, Bhattacharya SC. Upgrading of biomass by means of torrefaction. Energy 1990;15:1175–9.

[3] Wattananoi W, Khumsak O, Worasuwannarak N. Upgrading of biomass by torrefaction and densification process. In: 2011 IEEE conference on clean energy and technology; 2011. pp. 209–12.

[4] Medic D, Darr M, Shah A, Potter B, Zimmerman J. Effects of torrefaction process parameters on biomass feedstock upgrading. Fuel 2012;91:147–54.

[5] Bourgois J, Guyonnet R. Characterization and analysis of torrefied wood. Wood Sci Technol 1988;22:143–55.

[6] Bourgois J, Bartholin MC, Guyonnet R. Thermal treatment of wood: analysis of the obtained product. Wood Sci Technol 1989;23:303–10.

[7] Broido A, Nelson MA. Char yield on pyrolysis of cellulose. Combust Flame 1975;24:263–8.

[8] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 2008;87:844–56.

[9] Jones JM, Bridgeman TG, Darvell LI, Gudka B, Saddawi A, Williams A. Combustion properties of torrefied willow compared with bituminous coals. Fuel Process Technol 2012;101:1–9.

[10] Fisher EM, Dupont C, Darvell LI, Commandré J-M, Saddawi A, Jones JM, et al. Combustion and gasification characteristics of chars from raw and torrefied biomass. Bioresour Technol 2012;119:157–65.

[11] Couhert C, Salvador S, Commandré J-M. Impact of torrefaction on syngas production from wood. Fuel 2009;88:2286–90.

[12] Deng J, Wang G, Kuang J, Zhang Y, Luo Y. Pretreatment of agricultural residues for co-gasification via torrefaction. J Anal Appl Pyrol 2009;86:331–7.

[13] Bridgeman TG, Jones JM, Williams A, Waldron DJ. An investigation of the grindability of two torrefied energy crops. Fuel 2010;89:3911–8.

[14] Repellin V, Govin A, Rolland M, Guyonnet R. Energy requirement for fine grinding of torrefied wood. Biomass Bioenergy 2010;34:923–30.

[15] Phanphanich M, Mani S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresour Technol 2011;102:1246–53.

[16] Bates R, Ghoniem A. Biomass torrefaction: modeling of volatile and solid product evolution kinetics. Bioresour Technol 2012;124:460–9.

[17] Ratte J, Fardet E, Mateos D, Héry J-S. Mathematical modelling of a continuous biomass torrefaction reactor: TORSPYD™ column. Biomass Bioenergy 2011;35:3481–95.

[18] Prins MJ, Ptasinski KJ, Janssen FJJ. More efficient biomass gasification via torrefaction. Energy 2006;31:3458–70.

[19] Park WC, Atreya A, Baum HR. Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis. Combust Flame 2010;157:481–94.

[20] Yan W, Hastings JT, Acharjee TC, Coronella CJ, Vásquez VR. Mass and energy balances Of wet torrefaction of lignocellulosic biomass †. Energy Fuels 2010;24:4738–42.

[21] Bergman PC, Kiel JHA. Torrefaction for biomass upgrading. In: 14th European biomass conference & exhibition; 2005. pp. 17–21.

[22] Chiueh P-T, Lee K-C, Syu F-S, Lo S-L. Implications of biomass pretreatment to cost and carbon emissions: case study of rice straw and Pennisetum in Taiwan. Bioresour Technol 2012;108:285–94.

[23] Chen W-H, Kuo P-C. Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. Energy 2011;36:6451–60.

[24] Chen W-H, Kuo P-C. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. Energy 2010;35:2580–6.

[25] Park S-W, Jang C-H, Baek K-R, Yang J-K. Torrefaction and low-temperature carbonization of woody biomass: Evaluation of fuel characteristics of the products. Energy 2012;45:676–85.

[26] Prins MJ, Ptasinski KJ, Janssen FJJ. Torrefaction of wood. Part 1. weight loss kinetics. J Anal Appl Pyrol 2006;77:28–34.

[27] Prins MJ, Ptasinski KJ, Janssen FJJG. Torrefaction of wood. J Anal Appl Pyrol 2006;77:28–34.

[28] Friedl A, Padouvas E, Rotter H, Varmuza K. Prediction of heating values of biomass fuel from elemental composition. Anal Chim Acta 2005;544:191–8.

[29] Basu P. Biomass gasification and pyrolysis: practical design and theory. Elsevier Inc; 2010. pp. 2–63.

[30] Prins MJ. Thermodynamic analysis of biomass gasification and torrefaction. Technische Universiteit Eindhoven; 2005.

[31] Hougen O, Watson K. Chemical process principles. USA: Jhon Wiley; 2005. pp. 65–120.

[32] Prins MJ, Ptasinski KJ, Janssen FJJ. Torrefaction of wood. Part 2. analysis of products. J Anal Appl Pyrol 2006;77:35–40.

[33] Bejan A. Advanced engineering thermodynamics. 3rd ed. 2006. pp. 113–65. New Jersey.